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(71) Applicant: W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US).

(72) Inventors: HEN, Jie; 10433 Popkins Court, Woodstock, MD 21163 (US). GUO, Yihong; 9545 Clocktower Lane, Columbia, MD 21046 (US).

(74) Agent: LOOPER, Valerie, E.; W.R. Grace & Co.-Conn., 7500 Grace Drive, Columbia, MD 21044 (US).

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(54) Title: THERMOPLASTIC BLOCK COPOLYMER WITH INHERENT ANTI-FOG PROPERTIES

(57) Abstract

Anti-fog packaging film can be made using polyether polyamide block copolymers. Exposure to a polar medium such as liquid or gaseous water improves the consistency of anti-fog behavior.

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Thermoplastic Block Copolymer with Inherent Anti-Fog Properties

Field of the Invention

This application relates to thermoplastic block copolymers which are extrudable and have inherent anti-fog properties, as well as a method for making articles with improved resistance to fogging. The preferred copolymers are polyether polyamide block copolymers which are also extrudable and heat sealable. This invention is particularly useful for making transparent packaging films.

Background of the Invention

Polyolefin films are used to make see-through plastic wraps and bags for meat, produce, and a variety of other products. Such films are particularly useful, for example, when it is important for a customer to identify the product from a distance or to gauge product quality. However, when an object is wrapped in an unmodified polyolefin plastic film and then subjected to rapid changes in humidity and temperature, the film has a tendency to become cloudy, or fog. For that reason, anti-fog properties are widely desired.

Anti-fog properties relate to the ability of the film surface to prevent or to dissipate the condensation of water vapor into small, discrete droplets on the surface of the film.

The food packaging industry almost exclusively uses surfactant additives to confer anti-fog properties on polyolefin film surfaces. The surfactants are added in sufficient quantity to make the polyolefin surfaces, which are normally hydrophobic, wettable. If water vapor condenses on the surface of the film, it tends to form a thin, transparent layer instead of the discrete, cloudy-looking droplets.

A variety of additives for use with various film-making materials are known.

See, for example, United States Patent No. 2,561,010, issued to Carson, which discloses the dispersion of various surfactants such as hydrophilic fatty acid esters and polyoxyethylene ethers in hydrophobic polymers used to make films, such as polyvinyl chloride, polyethylene, and cellulose acetate.

United States Patent No. 5,149,724, issued to Fahey et al. September 22, 1992 relates to the use of a polyglycerol monoester and an ethoxylated sorbitan ester incorporated in a polyvinyl chloride or polyolefin thin film. The resulting film is said to have enhanced anti-static, anti-fog and dynamic heat stability properties. The reference points out that these properties are maintained at lower loadings than necessary for conventional anti-fogging additives. (Col. 1, lines 62-63).

United States Patent No. 3,541,040, issued to Eastes et al. November 17, 1970 relates to a blend of additives including sodium dioctyl sulfosuccinate, glycerol monostearate, and ethoxylated lauryl alcohol for use in a polyolefin film.

United States Patent No. 3,542,713, issued to Gillio-Tos et al. November 24, 1970 relates to the addition of polyoxyalkylene monoesterified with a fatty acid and a poly-alcohol esterified with a fatty acid to a poly(vinyl chloride) film.

This approach of using surfactant additives has a drawback in that the added surfactant may migrate and interfere with the physical properties of the film such as machinability and printability, as well as ultimate product performance such as shelf life of the product. Further, in the case of food packaging, the additive may not be approved under the various food laws. As a consequence, a polymeric material which is both extrudable and has anti-fog properties would be highly desirable.

Other methods of conferring anti-fog properties on other types of polymer surfaces are also known. For example, United States Patent No. 4,551,484, issued to Radisch et al. November 5, 1985, relates to a transparent coating or film for the eyeshields of motorcycle helmets. A thermosetting polyurethane article is soaked in a surfactant solution for at least a half hour and then is preferably waxed. The thermosetting polyurethanes are not extrudable (they solidify upon exposure to heat) and are not sealable. These factors are important because packaging films are commonly made by extrusion through a die into a very thin layer, and bags or wrapped packages are commonly sealed using heat. Any method of reducing a film's tendency to fog must not interfere with its extrudability or heat sealability. As a result, thermosetting polymers are generally not appropriate for use as a surface coating for packaging films. Further, the extended soaking process disclosed in this reference is slow and would represent significant cost increases in an extrusion process, due to the delay.

The present invention relates to an polymer composition which is extrudable, heat sealable, and also has inherent anti-fog properties. The composition is made of a polyether polyamide block copolymer, and can be used to make either monolayer or multilayer transparent films with surfaces that resist fogging. Such films are particularly useful to the packaging industry.

Various kinds of polyether polyamide block copolymers are known, such as those disclosed in United States Patent No. 4,252,920 issued to Deleens, et al. February 24, 1981, and in United States Patent No. 4,361,680 issued to Borg et al. November 30, 1982. Both patents are incorporated in this document by reference as if set forth in full.

These materials are known for use in films. See Brochure, "New Hydrophilic Polyether-Ester-Amide Block Copolymers" available from Atochem North America Polymers Division, Philadelphia, PA.

Objects and Advantages of the Invention

It is an object of the present invention to produce a polymeric film-forming material which has inherent anti-fog properties. It is a further object of the invention that the polymeric material be transparent, extrudable, and heat sealable. An advantage of the present invention is that films with surfaces made from the polymeric material need not contain surfactant additives to confer anti-fog properties, and may thereby avoid the side effects of the additives. Further objects and advantages will become apparent to the reader of this document.

Summary of the Invention

The present invention relates to a film having inherent anti-fog properties, and a method for making such a film. The film is made at least in part from a polyether polyamide block copolymer.

A preferred block copolymer is a polyether polyamide block copolymer having an overall molecular weight of 10,000 to 1,000,000, and an polyether:polyamide weight ratio of 80:20 to 20:80. The polyether blocks have a block molecular weight of 500 to 5,000, and are preferably made of polyethylene oxide groups. The polyamide blocks have a block molecular weight of 500 to 5,000, and are preferably poly(ω-dodecanolactam) groups.

The film may be conditioned by exposure to a polar medium, such as liquid or gaseous water. The conditioning step tends to improve the consistency of anti-fog behavior.

Brief Description of the Drawings

Fig. 1 is a photograph showing the results of the fog test from Example 1 comparing a polyolefin film without any surfactant additive, a surfactant-containing film, and the present invention.

Detailed Description of the Invention

The conventional approach to the problem of reducing the tendency of plastic films (or other objects) to fog has been to apply a surface chemical treatment or else to make the surface hydrophilic by using surfactant additives, so that condensed water spreads and forms a continuous layer instead of tiny droplets (fog) on the surface. In this invention, an intrinsic anti-fog polymer composition, without any surfactant additives, is used to obtain excellent anti-fog properties. This polymer can be used in a multilayer film with other layers of polymers that provide other useful properties such as thermal resistance, abuse resistance, and oxygen and moisture barrier.

The Block Copolymer

Films made according to the present invention are made at least in part from a block copolymer having a hydrophilic block (A) and a less hydrophilic block (B). The preferred block copolymer is the product obtained from the polycondensation of polyether blocks having reactive extremities with polyamide blocks having reactive extremities. This type of polymer has been variously referred to in the literature as poly(ether-*block*-amide), ether amide block copolymer, polyether polyamide block copolymer, or polyether polyamide block polymer.

One non-limiting method of forming a polyether polyamide block copolymer to be used as a thermoplastic inherent anti-fog material is by polycondensation of predominantly polyoxyalkylene having hydroxyl end groups with polyamide having carboxylic acid end groups, as illustrated in US Patent 4,252,920. This method produces an ester linkage between the polyamide and polyether blocks.

Another non-limiting method of forming such a block copolymer is by polycondensation of predominantly polyoxyalkylene having carboxylic acid end groups with polyamide having amine end groups. This method produces an amide linkage between the polyamide and polyether blocks. Both of these two methods were illustrated in US Patent 4,361,680.

The preferred polyether block (block A) is polyoxyalkylene, and more preferably, a polyethylene oxide group. Block A can include other polyether groups made by copolymerizing ethylene oxide with other monomers such as propylene oxide. The arts of polymerization and copolymerization of ethylene oxide are well known. See: Encyclopedia of Polymer Science and Engineering, John Wiley & Sons (1986) Vol. 6, p. 225.

The preferred polyamide block (block B) is a poly(ω-dodecanolactam) group. The homopolymer of poly(ω-dodecanolactam) is commonly known as nylon-12. Block B can include other polyamide groups made by the copolymerization of dodecanolactam or ω-aminododecanoic acid with other monomers. The arts of polymerization and copolymerization of amides are well known. See: Encyclopedia of Polymer Science and Engineering, John Wiley & Sons (1986), Vol. 11, p. 315.

The copolymer has an overall weight average molecular weight (In this document, the term "molecular weight" refers to weight average molecular weight unless otherwise specified.) of 10,000 to 1,000,000, preferably about

20,000 to 40,000. The blocks are present in a polyether:polyamide weight ratio of about 80:20 to 20:80, preferably a weight ratio of 40:60 to 60:40, and more preferably about 50:50.

Polyether polyamide block copolymers are especially suitable for use in packaging films, as they have inherent anti-fog properties, can be made to be compatible with the thermoplastic materials used to make multilayer film structures, are extrudable, and heat-sealable. Suitable commercially available polyether polyamide block copolymers are marketed under the trade-name Pebax (available from Elf Atochem North America, Inc., Birdsboro, PA).

The preferred block molecular weight range for the polyether is 500 to 5,000, preferably 1,000 to 2,000. The preferred block molecular weight for the polyamide is also 500 to 5,000, more preferably 1,000 to 2,000.

The block copolymer may be further combined with one or more polymeric diluents, such as thermoplastic polymers which are typically used to form film layers in plastic packaging articles. Polymers which can be used as the diluent include, but are not limited to, polyethylene terephthalate (PET), polyethylene of any density, polypropylene, polyvinyl chloride, polyvinylidine chloride, polyamide, polyether, polystyrene, and ethylene copolymers such as ethylene-vinyl acetate, ethylene-alkyl (meth)acrylates, ethylene-(meth)acrylic acid and ethylene-(meth)acrylic acid ionomers. In rigid articles such as beverage containers PET is often used. Blends of different diluents may also be used. The selection of the polymeric diluent largely depends on the article to be manufactured and the end use. Such selection factors are well known in the art.

Further non-surfactant additives may also be included in the composition to impart properties desired for the particular article being manufactured. Such additives include, but are not necessarily limited to,

fillers, pigments, dyestuffs, antioxidants, stabilizers, processing aids, plasticizers, fire retardants, etc.

Using the Block Copolymer to make Film

The copolymer can be formed into a monolayer or multilayer film by the usual methods, including hot pressing, extrusion, coextrusion, extrusion coating, solution coating, lamination, extrusion lamination, and combinations thereof. The anti-fog polymer needs to be physically located on the surface which is vulnerable to fogging, usually what will ultimately become either an outer or a product contact surface of the final product.

One of ordinary skill in the art will recognize that although this document is written in terms of the thin, transparent packaging films desired by the inventors, an extrudable block copolymer with inherent anti-fog properties would be useful to make anti-fog surfaces on a variety of objects, including those made of plastics, glasses and metals. Examples could include goggles, windows and mirrors.

Exposure of the film to a polar medium before packaging improves the consistency of the anti-fog behavior. This can be conveniently done by, for example, running an extruded film through a water bath or between water-saturated spongy rollers, passing the film through a steam or controlled humidity chamber, or passing the film between glass rollers.

EXAMPLES

The following Examples illustrate the practice of the present invention without limiting it, or limiting the Claims which follow.

Comparative Example 1

Pure polyethylene glycol (from Union Carbide, Danbury, CT) was dried and pressed in a CARVER heated lab press at 70°C. The resulting film became tacky upon exposure to water and dissolved.

Comparative Example 2

In this example, nylon-12 (available from Huls, Piscataway, NJ) was used alone. A 0.003-0.004 inch thick flexible film was prepared by pressing 20 grams pre-dried nylon-12 in a CARVER heated lab press at 190°C. The film was cut into two pieces, and one piece was washed with deionized water. To test for anti-fog properties, each piece was wrapped around the top of a 600 mL beaker containing 400 mL deionized water. The beakers were set side-by-side at 4°C overnight. Water condensed in the form of discrete water droplets (fog) on both pieces.

Comparative Example 3

In this example, poly(ethylene-oxide) (Polysciences, Warrington, PA, M.W. = 300,000) and poly(ethylene-oxide-co-propylene-oxide) (Polysciences, Warrington, M.W.=13,300, the ratio of ethylene-oxide to propylene-oxide was 3) were tested.

A 0.003-0.004 inch thick flexible film was prepared by pressing 20 grams pre-dried polymer sample in a CARVER heated lab press at 140°C. Each sample was wrapped around the top of one 600 mL beaker containing 400 mL deionized water and chilled to 4°C. After a few hours, the poly(ethylene-oxide) film was swollen, cloudy and covered with discrete water droplets. The poly(ethylene-oxide-co-propylene-oxide) film was covered with discrete water droplets.

Example 1

Anti-fog properties of a commercially available unmodified hydrophobic film, a commercially available surfactant-containing anti-fog film, and the present invention were compared. The unmodified hydrophobic polymer sample was SSD310 polyolefin film from Cryovac Division of W. R. Grace & Co.-Conn., Duncan, SC. The commercially available anti-fog film

was AFG film containing glycol mono-stearate from DuPont De Nemours, Wilmington, DE. The copolymer of the present invention was pre-dried PEBAX MX1074 (an alternating block copolymer consisting of polyethylene oxide groups and poly(ω-dodecanolactam) groups which has a total molecular weight of 30,000 to 40,000, a molecular weight for each block of 1,450 to 1,500, and which is available from Elf Atochem)

A sample of 0.003-0.004 inch thick flexible film was prepared from the copolymer of the present invention by pressing about 20 grams polymer in a CARVER hot press at 170°C. The commercially available films were used as is. Pieces of film were used to cover the tops of 600 ml beakers containing 400 ml of water. The beakers set side-by-side on top of a sheet with a printed pattern at 4°C overnight. The results are shown in Fig. 1. The unmodified hydrophobic film was covered with minute, discrete droplets (heavily fogged) so that the pattern under the beaker was barely visible. The commercially available anti-fog film is covered with large, loose droplets which interfered with the visibility of the pattern. The film of the present invention had no droplets, and the pattern was sharp and clearly visible through it.

Example 2

A sample of a film made of a batch of pre-dried PEBAX MX1074 different from the batch used in Example 1, one that failed a seven day, low-temperature (4°C) fog test, was conditioned and retested. The sample was cut into two pieces, and one piece was washed with water.

For the fog test, the above two film pieces were wrapped around the top of two 600 mL beakers containing 400 mL deionized water. The beakers were set side-by-side at a temperature of 4°C and observed periodically for seven days. The piece which had been washed remained transparent and had no water droplets on it, while the piece which had not been washed with water turned cloudy.

Example 3

Another sample of the same PEBAX MX1074 film used in Example 2 was cut into two pieces. One piece of the film was exposed to 50% RH (relative humidity) at 25°C for four hours. Then, each piece was wrapped around the top of a 600 mL beaker containing 400 mL deionized water. The piece without moisture exposure turned cloudy, while the piece with moisture exposure showed excellent anti-fog behavior. That is, it remained transparent and had no visible water droplets on its surface throughout seven days in the anti-fog test at 4°C.

Example 4

The following formulation was prepared in a Brabender mixing chamber: 35 grams of PEBAX MX1074 was mixed with 15 grams of silica (Aerosil 200, Degussa), for 20 min. at a temperature of 200°C. A 0.003-0.004 inch thick flexible film was prepared by pressing 20 grams the above blend in a Carver hot press at 170°C. The film was wrapped around the top of a 600 mL beaker containing 400 mL deionized water. It showed excellent anti-fog behavior. That is, it remained transparent and had no visible water droplets on its surface throughout seven days in the anti-fog test at 4°C.

Example 5

The following formulations were prepared in a Brabender mixing chamber by blending a total of 50 grams of material in the manner of Example 4 for 20 min. at a temperature of 200°C. The figures given are in weight percent of total formulation. A 0.003-0.004 inch thick flexible film was prepared of each formulation by pressing 20 grams of the blend in a Carver hot press at 170°C.

TABLE 1

Ingredients	A	B	C	D
PEBAX MX1074	40%	30%	30%	
EVA[1]	40%	40%	40%	
LLDPE[2]	20%	20%		
silica		10%		10%
PEBAX MX1041[3]			30%	90%

[1] ethylene vinyl acetate with 28% vinyl acetate, available from Dow Chemical Co.
[2] Linear low density polyethylene, available from Dow Chemical Co.
[3] An alternating block copolymer consisting of polyethylene oxide groups and poly(ω-dodecanolactam) groups, which has a total molecular weight (MW) of 30,000 to 40,000, a molecular weight for polyethylene oxide of about 1,000 for poly(ω-dodecanolactam) of about 2,000, available from Elf Atochem.

The films were wrapped around the top of a 600 mL beaker containing 400 mL deionized water. All showed excellent anti-fog behavior. That is, each remained transparent and had no visible water droplets on its surface throughout seven days in the anti-fog test at 4°C.

What is Claimed is:

1. A method of making an article having an inherent anti-fog properties, comprising forming a film having an outer surface, the surface comprising a polyether polyamide block copolymer having a polyether:polyamide weight ratio of 80:20 to 20:80.

2. The method of Claim 1, wherein the polyether block has a weight average molecular weight of 500 to 5,000.

3. The method of Claim 1, wherein the polyether block has a weight average molecular weight of 1,000 to 2,000.

4. The method of Claim 1, wherein the polyamide block has a weight average molecular weight of 500 to 5,000.

5. The method of Claim 1, wherein the polyamide block has a weight average molecular weight of 1,000 to 2,000.

6. The method of Claim 1, wherein the polyether:polyamide weight ratio is 40:60 to 60:40.

7. The method of Claim 1, wherein the polyether:polyamide weight ratio is about 50:50.

8. The method of Claim 1, wherein the polyether block is a polyethylene oxide group.

9. The method of Claim 1, wherein the polyamide block is a poly(ω-dodecanolactam) group.

10. The method of Claim 1, wherein the copolymer is an alternating block copolymer of polyethylene oxide groups and poly(ω-dodecanolactam) groups, or mixtures thereof, wherein the block copolymer has a total weight average molecular weight of 30,000 to 40,000, and a weight average molecular weight for each block of 1,450 to 1,500.

11. The method of Claim 1, wherein the surface further comprises a polymeric diluent.

12. The method of Claim 1, wherein the polymeric diluent is selected from the group consisting of ethylene vinyl acetate and linear low density polyethylene.

13. The method of Claim 1, wherein the surface further comprises a filler.

14. The method of Claim 1, wherein the filler is silica.

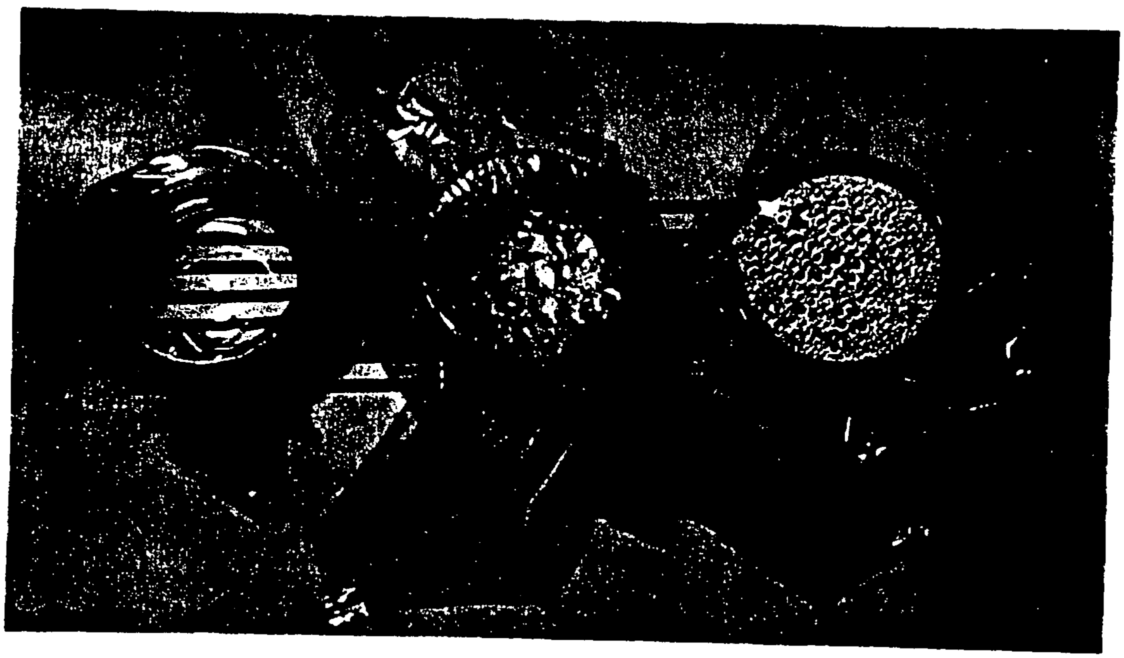
15. The method of Claim 1, further comprising the step of conditioning the film surface by exposure to a polar medium.

16. The method of Claim 15, wherein the film is conditioned by exposure to at least 50% humidity.

17. The method of Claim 15, wherein the film is conditioned by exposure to liquid water.

18. An article comprising a film made by the method of any one of Claims 1 - 17.

19. An article having a coating made by the method of any one of Claims 1-17.



INVENTION SURFACTANT-CONTAINING FILM POLYETHYLENE FILM

FIG. 1

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 96/00514

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G69/40 C08L77/00 C08L77/08 C08J7/02 //(C08L77/00, 23:04),(C08L77/00,31:04)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 506 495 (ATOCHEM ELF SA) 30 September 1992 ---	
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A	EP,A,0 559 284 (ENICHEM POLIMERI) 8 September 1993 ---	
A	DATABASE WPI Section Ch, Week 8436 Derwent Publications Ltd., London, GB; Class A23, AN 84-223067 XP002003638 & JP,A,59 133 224 (UBE INDUSTRIES KK) , 31 July 1984 see abstract -----	

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 May 1996	05.06.96

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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